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**Patentanmeldung Nr.    Patent application No.    Demande de brevet n°**

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Der Präsident des Europäischen Patentamts;  
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets  
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Block copolyetherester elastomer and preparation thereof

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BLOCK COPOLYETHERESTER ELASTOMER AND PREPARATION THEREOF

5                   The invention relates to a block copolyetherester elastomer comprising polyester hard blocks and poly(alkylene oxide) blocks, obtainable by esterification of at least one aromatic dicarboxylic acid or an ester-forming derivative thereof, at least one alkylene diol, and a poly(alkylene oxide) polyol, comprising an poly(propylene oxide) end capped with ethylene oxide. The invention further relates to  
10 a process for the preparation of a block copolyetherester elastomer comprising polyester hard blocks and poly(alkylene oxide) blocks wherein at least one aromatic dicarboxylic acid or an ester-forming derivative thereof, at least one alkylene diol, and a poly(alkylene oxide) polyol, comprising an poly(propylene oxide) end capped with ethylene oxide, are esterified.

15                   A block copolyetherester elastomer as described above is known from EP-B-203634. The known elastomer is made of dimethyl terephthalate (DMT), 1,4-butane diol and poly-1,2-propylene oxide glycol capped with ethylene oxide. The known elastomer has a number average molecular weight of 2370 kg/mol and an ethylene oxide content of 20% by weight.

20                   A disadvantage of the known elastomer is that its modulus and hardness are too high for applications such as highly elastic fibers and films.

                  A general approach for reducing the modulus and hardness of block copolymers in general is by increasing the number of "soft blocks". For block copolyetherester elastomers this would mean that the number of polyalkyleneoxide  
25 blocks, which act as soft blocks in said elastomers, would have to be increased to reduce the modulus and hardness. However, if this approach is applied for modifying the known elastomer, the mechanical properties, in particular the elongation-at-break, deteriorate.

                  The aim of the invention is to provide an elastomer having reduced  
30 modulus and hardness compared to the known elastomer, while retaining a sufficiently high elongation at break.

                  This aim has been achieved with the block copolyetherester elastomer according to the invention, wherein

- a. the poly(alkylene oxide) polyol has a Mn of between 2500 and 5000 g/mol;
- 35 b. the poly(alkylene oxide) polyol has an poly(ethylene oxide) content of between 22 and 90 % by weight;
- c. the ratio by weight of poly(alkylene oxide) polyol/aromatic dicarboxylic acid or an

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ester-forming derivative thereof is between 60/40 and 90/10;

- d. the average degree of polymerization of the hard polyester block is at least 3.5;
- e. the block copolyetherester elastomer has an unsaturation content, being the total content of vinyl and allyl groups, of less than 25 meq per kg of the poly(alkylene oxide) polyol;
- f. the block copolyetherester elastomer has a Mn of at least 25,000 g/mol.

The block copolyetherester elastomer according to the invention surprisingly features a significantly reduced modulus and Shore A hardness, while the elongation at break is retained at the same level or even improved compared to the known elastomer. Another surprising advantage of the block copolyetherester copolymer according to the invention is that it shows a high moisture vapour transmission rate (MVTR).

The block copolyetherester elastomer according to the invention comprises polyester blocks as "hard blocks" and polyalkylene oxide blocks as "soft blocks".

The hard polyester blocks are built up from repeating units derived from at least one alkylene diol and at least one aromatic dicarboxylic acid or an ester-forming derivative thereof. The alkylene diol contains generally 2-6 C-atoms, preferably 2-4 C-atoms. Examples thereof include ethylene glycol, propylene diol and butylene diol. Preferably, 1,4-butylene diol is used. Examples of suitable aromatic dicarboxylic acids include terephthalic acid, 2,6-naphthalenedicarboxylic acid, 4,4'-biphenyldicarboxylic acid or combinations of these. The hard segments may optionally further contain a minor amount of units derived from other dicarboxylic acids, for example isophthalic acid, which generally lowers the melting point of the polyester. The amount of other dicarboxylic acids is preferably limited to not more than 10 mol%, more preferably not more than 5 mol%, so as to ensure that, among other things, the crystallization behaviour of the copolyetherester is not adversely affected. The hard segment is preferably built up from ethylene terephthalate, propylene terephthalate, and in particular from butylene terephthalate as repeating units. Advantages of these readily available units include favourable crystallisation behaviour and a high melting point, resulting in copolyetheresters with good processing properties and excellent thermal and chemical resistance. In other preferred embodiments of the process according to the invention, the hard segments in the copolyetherester are built up from units derived from ethylene glycol, 4,4'-biphenyldicarboxylic acid, terephthalic acid and/or 2,6-naphthalenedicarboxylic acid, and optionally minor amounts of other diacids and/or diols. These copolyetheresters show a high crystalline melting point, and fast

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crystallisation upon cooling from the melt.

The soft polyalkyleneoxide blocks comprise poly(propyleneoxide) end capped with ethylene oxide. With a poly(propyleneoxide) end capped with ethylene is indicated a tri-block copolymer with a poly(propylene oxide) (PPO) as the central block, and two end blocks of poly(ethylene oxide) (PEO). Advantages of such a polyether as soft block include its hydroxyl functionality and good reactivity and compatibility in the synthesis of polyether esters.

Preferably the poly(alkylene oxide) polyol is a diol. Herein diol is understood to mean that the poly(alkylene oxide) polyol has essentially hydroxyl groups as end groups; that is it has a hydroxyl functionality of about 1.7-2.3. A lower functionality would hamper synthesis of a block copolyetherester elastomer of sufficiently high molar mass; a higher functionality would undesirably increase chain branching or even induce cross-linking of the block copolyetherester elastomer. The hydroxyl functionality is therefore preferably 1.8-2.2, more preferably 1.9-2.1, and even more preferably about 2.

The poly(alkylene oxide) polyol used in the block copolyetherester elastomer according to the invention has an Mn of between 2500 and 5000 g/mol, preferably between 2800 and 5000 g/mol, more preferably between 3000 and 5000 g/mol. The use of high Mn poly(alkylene oxide) polyol instead of conventional lower Mn poly(alkylene oxide) polyols results in polyalkyleneoxide blocks with a relatively high Mn and consequently a relatively high length. By using such "long" polyalkyleneoxide blocks it is possible to increase the content of soft blocks in the block copolyetherester elastomer and thereby soften the block copolyetherester copolymer, while keeping the polyester blocks long enough to still obtain polyester crystallization. It is important that polyester crystallization occurs in the block copolyetherester elastomer according to the invention. Easily destroyable small irregular polyester crystallites may furthermore contribute to irreversible deformation, having a negative effect on the recoverability of the block copolyester. Furthermore, insufficient crystallization of the polyester hard block may result in an undesirably low melting point/crystallization temperature of the block copolyetherester elastomer. For some applications, for example fiber spinning, a high crystallization temperature is crucial. Optionally the crystallization temperature of the block copolyetherester elastomer may be increased by the addition a nucleating agent. Nucleating agents are sometimes also referred to as crystallisation improvers or crystallisation promoters. In general, suitable nucleating agents for the present copolyetherester composition include those already known in the art, especially for polyesters, like poly(ethylene terephthalate). Suitable agents include inert particulate



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nucleating agents, metal salts of monocarboxylic acids and dicarboxylic acids; metal salts of aromatic carboxylic acids such as benzoic acid; hydrous magnesium silicates such as talcum, and aluminium silicates such as clay; polyol acetals such as substituted sorbitol; metal salts of organophosphates such as sodium di(4-t-butylphenyl) phosphate, and others. Suitable examples of metal salts of a carboxylic acids, are potassium, lithium or sodium salts. Preferably, a sodium salt of a carboxylic is chosen as nucleating agent in view of handling and effectiveness. Examples of such acids, the metal salts of which may be used as nucleating agents, include formic, acetic, propionic, butyric, valeric, caproic, caprylic, capric, lauric, itaconic, myristic, palmitic, stearic, oleic, linoleic, linolenic, cyclohexanecarboxylic, phenylacetic, benzoic, o-toluic, m-toluic, p-toluic, o-chlorobenzoic, m-chlorobenzoic, p-chlorobenzoic, o-bromobenzoic, m-bromobenzoic, p-bromobenzoic, o-nitrobenzoic, m-nitrobenzoic, p-nitrobenzoic, phthalic, isophthalic, terephthalic, salicylic, p-hydroxybenzoic, anthranilic, m-aminobenzoic, p-aminobenzoic, o-methoxybenzoic, m-methoxybenzoic, p-methoxybenzoic (anisic), oxalic, malonic, succinic, glutaric, adipic, maleic and fumaric acid. Preferred metal salts of carboxylic acids include sodium stearate and sodium benzoate. Also, fine mineral particles such as hydrous magnesium silicates (talcum) and hydrous aluminum silicates (clay) function as inert particulate nucleating agents suitable for use in the practice of the present invention. Preferably, talcum of average particle size below 150 micrometer ( $\mu\text{m}$ ), below 100  $\mu\text{m}$  or even below 50  $\mu\text{m}$  is chosen as nucleating agent.

In a preferred embodiment of the invention, talcum particles of particle size 0,01 – 40  $\mu\text{m}$  are used, more preferably of particle size 0,01 – 25  $\mu\text{m}$ , which particles have been melt-dispersed into a carrier material, preferably a copolyetherester, optionally in a concentration higher than the desired concentration in the block copolyetherester elastomer. Such a concentrate of nucleating agent can be easily blended with the block copolyetherester elastomer and optionally other additives. The advantage of this concentrate route is a better control over dispersion of nucleating agent particles and homogeneous distribution thereof in the composition, which results in further improving the consistency and reproducibility of the process according to the invention.

Preferably, the block copolyetherester elastomer according to the invention comprises 0,02 – 1 mass% of nucleating agent, more preferably 0,05 – 0,5 or 0,07 – 0,25 mass%.

The poly(alkylene oxide) polyol has an poly(ethylene oxide) content of between 22 and 90 % by weight, preferably between 30 and 70 % by weight, more

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preferably between 40 and 60 % by weight, and most preferably between 45 and 55 % by weight. Preferably the amount of poly(ethylene oxide) in the poly(alkylene oxide) polyol and the Mn of the poly(alkylene oxide) polyol are chosen such that during the esterification reaction no macrophase separation occurs, which would deteriorate the mechanical properties of the block copolyetherester elastomer. Macrophase separation occurs when the hard and soft segments are no longer compatible with one another under the conditions of melt condensation. This leads to a two phase morphology of the copolyetherester on a relatively large scale (micrometer), with one phase rich in soft segments and the other rich in hard segments. Macrophase separation is defined in for example "Thermoplastic elastomers", N.R.Legge, G. Holden, H.E. Schroeder, Carl Hanser Verlag, Munich, 1987. It is generally known that a higher poly(ethylene oxide) content results in a better mixing of polyester and the poly(alkylene oxide) polyol, which reduces the tendency for macrophase separation. On the other hand, a too high poly(ethylene oxide) content may lead to poly(ethylene oxide) crystallization, which can limit the low temperature performance. Therefore, the poly(ethylene oxide) content is balanced to avoid macrophase separation and poly(ethylene oxide) crystallization as much as possible.

The ratio by weight of poly(alkylene oxide) polyol/aromatic dicarboxylic acid or an ester-forming derivative thereof is between 60/40 and 90/10. The preferred amount depends on the Mn of the poly(alkylene oxide) polyol, i.e. the higher the Mn of the poly(alkylene oxide) polyol the more poly(alkylene oxide) polyol can be incorporated in the block copolyetherester elastomer without destroying too much of the polyester crystallinity. In order to obtain a block copolyetherester elastomer with a high elasticity and softness, it is generally preferable to apply the highest possible ratio of poly(alkylene oxide) polyol/aromatic dicarboxylic acid or an ester-forming derivative thereof which still gives sufficient polyester crystallization.

If the polyester is polybutylene terephthalate (PBT), the amount of poly(alkylene oxide) polyol which can be incorporated into a block copolyetherester elastomer while retaining sufficient PBT crystallization can be calculated from the overall length of the poly(alkylene oxide) polyol. Figure 1 shows a plot of the average number of butylene terephthalate units per PBT block as a function of the amount of poly(alkylene oxide) polyol in the block copolyetherester elastomer. Herein it is assumed that the length of a PBT block in average should contain at least four butylene terephthalate units to still obtain PBT crystallinity (H. Schroeder and R.J. Chella, Elastic Polymers, Encycl. Polym. Sci. Eng., 12 (1986), p. 75). Figure 1 shows for example that the maximum amount of poly(alkylene oxide) polyol which is possible

to incorporate into the block copolyetherester copolymer is about 84 % for a poly(alkylene oxide) polyol with  $M_n = 4600$  g/mol, about 82 % for a poly(alkylene oxide) polyol with  $M_n = 4000$  g/mol, about 79 % for a poly(alkylene oxide) polyol with  $M_n = 3300$ , about 77% for a poly(alkylene oxide) polyol with  $M_n = 3000$  or 2800 and about 71% for a poly(alkylene oxide) polyol with  $M_n = 2200$ . Therefore, the ratio by weight of poly(alkylene oxide) polyol/ PBT is preferably equal to or smaller than 90/10 when  $4000 < M_n(\text{poly(alkylene oxide) polyol}) \leq 5000$  g/mol, preferably equal to or smaller than 82/18 when  $3300 < M_n(\text{poly(alkylene oxide) polyol}) \leq 4000$  g/mol, preferably equal to or smaller than 79/21 when  $3000 < M_n(\text{poly(alkylene oxide) polyol}) \leq 3300$  g/mol, and preferably equal to or smaller than 77/23 when  $2500 \leq M_n(\text{poly(alkylene oxide) polyol}) \leq 3000$  g/mol.

The average degree of polymerization of the polyester block is at least 3.5. The average degree of polymerization of PBT is the average number of butylene terephthalate monomer units in the PBT blocks of the blockcopolymer. If the average degree of polymerization is lower than 3.5 the block copolyetherester elastomer material may not crystallize to a sufficient amount and show bad mechanical properties.

The block copolyetherester elastomer has a unsaturation content of less than 25 meq per kg of the poly(alkylene oxide) polyol, preferably less than 20 meq per kg of the poly(alkylene oxide) polyol and more preferably less than 15 meq per kg of the poly(alkylene oxide) polyol. Conventional poly(alkylene oxide) polyols with a high amount of unsaturated end groups (vinyl and allyl) usually result in a low molecular weight of the block copolyetherester elastomer as the unsaturated end groups act as chain stoppers in the polycondensation reaction. Such low molecular weight block copolyetherester elastomers usually feature a low strain at break. The poly(alkylene oxide) polyol used in the block copolyetherester according to the invention has a low unsaturation content and has a high reactivity, resulting in a high molecular weight of the block copolyetherester elastomer after a relatively short copolymerization time. It has thus been found that the block copolyetherester elastomer according to the invention, obtainable by using a poly(alkylene oxide) polyol with a high  $M_n$  and a low amount of unsaturated end groups, has a sufficiently high molecular weight and improved elasticity, softness and mechanical properties.

The  $M_n$  of the block copolyetherester elastomer can be calculated from the end groups, i.e. unsaturations, COOH and OH groups, and is expressed in meq/kg of the block copolyetherester elastomer.

For the molecular weight following formula holds:

$$M_n [g/mol] = \frac{10^6}{\sum EG[meq/kg]/2}$$

- 5 wherein EG = endgroups (COOH, OH, unsaturation).

The block copolyetherester elastomer has an Mn of at least 25,000 g/mol, preferably at least 30,000 g/mol, more preferably at least 35,000 g/mol. As explained above, the Mn of the block copolyetherester elastomer is among other  
10 dependent on the unsaturation content of the poly(alkylene oxide) polyol used for the soft block. A higher Mn usually results in improved mechanical properties, as can be seen from the examples.

The copolyetherester composition may further comprise any customary additives, like heat- and UV-stabilisers, anti-oxidants, colorants, processing  
15 aids like mould release agents or melt-flow enhancers, or mineral fillers. Preferably, the composition contains an effective amount of a heat-stabilisation and anti-oxidant package in view of the relatively long residence times in the melt, that are encountered during making of a preform. Generally, the total amount of such additives is less than 10 mass%, preferably about 0,05 – 5 or 0,1 - 3 mass% based on the total composition  
20 is applied.

Preferably the block copolyetherester elastomer according to the invention has a high moisture vapour transmission rate (MVTR), in order to be suitable for use in for example breathable films. The MVTR can be measured according to ASTM E96B (wet cup, 38 °C, 50 % relative humidity), resulting in the MVTR(E96B),  
25 and according to ASTM E96BW (inverted cup 38 °C, 50 % relative humidity), resulting in MVTR(E96BW). The MVTR(E96B) and the MVTR(E96BW) increase with increasing amount of polyalkylene oxide in the block copolyetherester elastomer and with increasing amount of poly(ethylene oxide) in the polyalkylene oxide. Preferably, the MVTR (E96B) is equal to or higher than 100 g.mm/m<sup>2</sup>.day, more preferably equal to or  
30 higher than 112 g.mm/m<sup>2</sup>.day, most preferably equal to or higher than 130 g.mm/m<sup>2</sup>.day. Preferably, the MVTR (E96BW) is equal to or higher than 550 g.mm/m<sup>2</sup>.day, more preferably equal to or higher than 900 g.mm/m<sup>2</sup>.day, most preferably equal to or higher than 1300 g.mm/m<sup>2</sup>.day.

The ShoreA hardness of the block copolyetherester elastomer according to the invention, measured according to DIN 53505, is dependent on the amount of polyalkylene oxide, the soft block, in the elastomer. For applications in which a high softness is required, for example elastic films of elastic fibers, a low ShoreA hardness of the block copolyetherester elastomer is desirable. Preferably the ShoreA hardness of the block copolyetherester according to the invention is equal to or lower than 92, more preferably equal to or lower than 87, in particular equal to or lower than 84, more in particular equal to or lower than 80.

The  $E'(23\text{ }^{\circ}\text{C})$  of the block copolyetherester elastomer according to the invention, measured according to ASTM D5026, is also dependent on the amount of polyalkylene oxide, the soft block, in the elastomer. Preferably the  $E'(23\text{ }^{\circ}\text{C})$  is equal to or lower than 50 MPa, more preferably equal to or lower than 30 MPa, in particular equal to or lower than 20 MPa, more in particular equal to or lower than 10 MPa.

The block copolyetherester elastomer according to the invention can be used in for example an elastic fiber or in an elastic film. Preferably the elastic film is breathable.

The invention also relates to a process for the preparation of a block copolyetherester elastomer comprising polyester blocks and polyalkylene oxide blocks, wherein at least one aromatic dicarboxylic acid or an ester-forming derivative thereof, one alkylene diol, and a poly(alkylene oxide) polyol, comprising an poly(propyleneoxide) end capped with ethylene oxide, are esterified, characterized in that

- a. the poly(alkylene oxide) polyol has a  $M_n$  of between 2500 and 5000 g/mol;
- b. the poly(alkylene oxide) polyol has an ethyleneglycol content of between 22 and 90 % by weight;
- c. the ratio by weight of poly(alkylene oxide) polyol/ aromatic dicarboxylic acid or an ester-forming derivative thereof is between 60/40 and 90/10;
- d. the average degree of polymerization of the polyester block is at least 3.5;
- e. the poly(alkylene oxide) polyol has an unsaturation content, being the total content of vinyl and allyl groups, of less than 25 meq per kg of the poly(alkylene oxide) polyol;
- f. the block copolyetherester elastomer has a  $M_n$  of at least 25,000 g/mol.

The process according to the invention can be carried out using any known method. Examples and preparation of copolyetheresters are for example described in Handbook of Thermoplastics, ed. O.Olabishi, Chapter 17, Marcel Dekker

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Inc., New York 1997, ISBN 0-8247-9797-3, in Thermoplastic Elastomers, 2nd Ed, Chapter 8, Carl Hanser Verlag (1996), ISBN 1-56990-205-4, in Encyclopedia of Polymer Science and Engineering, Vol. 12, Wiley & Sons, New York (1988), ISBN 0-471-80944, p.75-117, and the references cited therein.

5 In the process according to the invention a compound with two or more functional groups may be used that can react with an acid- or hydroxyl-group, acting as chain extension or chain branching agent, respectively. Examples of suitable chain extension agents include carbonylbisactams, diisocyanates and bisepoxides. Suitable chain branching agents include e.g. trimellitic acid, trimellitic acid anhydride and trimethylol propane. The amount and type of chain extension or branching agent is 10 chosen such that a block copolyetherester of desirable melt viscosity is obtained. In general, the amount of a chain branching agent will not be higher than 6.0 equivalents per 100 moles of dicarboxylic acids present in the copolyetherester.

15 In a preferred embodiment of the process according to the invention the esterification reaction is performed in the presence of up to 6.0 equivalents per 100 moles of dicarboxylic acid of a diisocyanate. More preferably, if diisocyanates are applied, said reaction in the melt, for example in an extruder, as the used diisocyanate may be too reactive to immediately add to the reactor.

20 The invention further relates to the use of the block copolyetherester elastomer according to the invention in an elastic fiber or an elastic, preferably breathable, film. The invention also relates to a product comprising at least one block copolyetherester elastomer according to the invention, in particular to an elastic fiber and an elastic film.

**Examples**Starting materials

- 5 Dimethylterephthalate (DMT) from BP Amoco, butanediol (BD) from BASF, Pluronic PE 6201 and PE9400 from BASF, Acclaim 4220 from Bayer and TB4040, A and B from Ineos, Arnitel PL380 from DSM, tetrabutyl titanate (TBT) from Fluka and magnesium acetate tetra hydrate ( $\text{Mg}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ ) from Aldrich were used as received.
- Information about the chemical compositions of the poly(alkylene oxide) polyols
- 10 (poly(alkylene oxide) polyol) used in the Examples and Comparative Experiments is given in Table 1.

Table 1: Molecular weights, compositions and amount of unsaturations of the investigated poly(alkylene oxide) polyols.

15

Poly(alkylene oxide) polyol	Mn (PEO) [g/mol]	Mn (PPO) [g/mol]	Mn (PEO) [g/mol]	Mn [g/mol] (overall)	%PEO/%PPO	Unsaturations [meq/kg]
A	680	1650	680	3000	45/55	10
B	830	1650	830	3300	50/50	9
Pluronic 6201 C	275	1750	275	2300	30/70	36
Pluronic 9400 D	925	2750	925	4600	40/60	57
Acclaim 4220 E	400	3200	400	4000	20/80	10
Ineos TB4040 F	580	1650	580	2800	40/60	27

General procedure for the preparation of block copolyetherester elastomer

- 20 DMT (150.8 g, 0.777 mol), BD (97.9g, 1.09mol), poly(alkylene oxide) polyol (0.139mol), catalyst TBT (384mg, 1.128mmol) and cocatalyst  $\text{Mg}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (241mg, 1.128mmol) were placed in a lab scale glass autoclave under nitrogen.

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The reaction mixture was heated slowly under stirring and a slight nitrogen flow from room temperature to 220 °C. The transesterification reaction started around 160 °C. The formed methanol was distilled off. Subsequently, the melt temperature was increased until 245 °C and excess BD distilled under vacuum (< 1mbar). The

5 polycondensation reaction was stopped after reaching the desired melt viscosity. The torque, being proportional to the melt viscosity, was measured by monitoring the electrical current required to maintain an agitation rate of 20 rpm. At the end of the reaction, the melt was released from the reactor under nitrogen pressure into a water bath and rolled up to form a thread. Subsequently, the thread was chopped into pellets,

10 ready for analysis and processing.

#### Viscometry

Viscometry was performed using a Ubbelohde capillary viscosimeter (Schott). The flow

15 time was determined using 10 wt-% in m-cresol at 25 °C. A correction according to Hagenbach was applied.

#### Carboxylic acid end groups analysis

20 The content of carboxylic end groups was determined by titration with potassium hydroxide, the equilibrium being determined with a Methrohm photometer E662.

#### OH end group analysis

25 OH end groups were determined by dissolution of the block copolyetherester elastomer together with internal standard 1-hexadecanol in 1,1,1,3,3,3-hexafluoro-2-propanol. Subsequently the hydroxyl groups were esterified by anthracenoylchloride. The solution was analyzed by HPLC, using UV detection.

#### 30 <sup>1</sup>H NMR

<sup>1</sup>H NMR was used to determine the unsaturated vinyl and allyl end groups and the PEO content in the poly(alkylene oxide) polyol. Analyses were performed on a Bruker ARX-400, using DMSO-d<sub>6</sub> as the solvent.

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DSC

- DSC measurements were performed on a Mettler DSC 821. The samples were heated from room temperature to 250 °C and kept at this temperature for 5 min. Subsequently
- 5 the samples were cooled to -120 °C with a holding time of 5 min and heated to 250 °C again. The rate of heating/cooling was 10 °C/min.

DMTA

- 10 The materials were pressed into films of 70x40 mm and a thickness of 0.08 mm using a standard pressing procedure ( $T \approx 240$  °C). From these films test samples were cut. The DMTA measurements in tension were performed on the RSA-II from Rheometrics according to ASTM D5026 using a frequency of 1 Hz. The temperature was varied from -130 to 240 °C with 5 °C/min.

15

Tensile Tests / Hysteresis tests

- Tensile and Hysteresis tests were performed on test bars (ISO 527-2), which were cut from 2 mm thick injection moulding plates (parallel to the injection moulding direction).
- 20 A Zwick tensile machine was used, which was equipped with the appropriate rubber clamps, a load cell of 2000N and optical sensors to measure the strain. All tests were performed with a speed of 100 mm/min. For the hysteresis tests the strain was increased by 25% for each cycle and the dwell time (waiting time at the end of each cycle) was set to 0 s. All tests were at least performed in 3 fold.

25

Moisture Vapor Transmission rate

- Moisture vapor transmission rates were measured on compression moulded films (ca 80 to 100  $\mu$ m), which have been prepared from granules using a standard pressing
- 30 procedure ( $T=240^{\circ}\text{C}$ ). The tests were performed according to ASTM E96B and E96BW at 38°C and 50% relative humidity. Temperature and humidity were controlled by a climate chamber from CTS.

**Examples I and II, Comparative experiments 1-4****Synthesis of the block copolyetherester elastomer**

- 5 Using different amounts of the poly(alkylene oxide) polyols A-F a series of block  
copolyetherester elastomers has been synthesized as described above. The amount of  
poly(alkylene oxide) polyols was increased up to the theoretically calculated limit for  
PBT crystallization for each soft block (see description). For each reaction the  
polycondensation time, the appearance of the melt, the torque at the end of the  
10 polycondensation (pc), the relative viscosity  $\eta_{rel}$ , the results of the end group analysis  
and the molecular weight calculated from the end groups are given in Table 2.  
Comparative Example 1 has a ratio by weight of poly(alkylene oxide) polyol/aromatic  
dicarboxylic acid or the ester forming derivative thereof of smaller than 60/40. In  
Comparative Example 2 poly(alkylene oxide) polyol C is used, which has a  $M_n$  smaller  
15 than 2500 g/mol. The unsaturations content is lower than 25 meq per kg of the  
poly(alkylene oxide) polyol. In comparative Example 3 poly(alkylene oxide) polyol D is  
used with an unsaturations content of lower than 25 meq per kg of the poly(alkylene  
oxide) polyol. Comparative Examples 4-6 use polyol E, which has an ethylene oxide  
content smaller than 22 wt%. Comparative Examples 7 and 8 apply poly(alkylene  
20 oxide) polyol F, which has an unsaturations content of more than 25 meq per kg of the  
poly(alkylene oxide) polyol.

- Table 2: Polycondensation time, appearance of the melt, torque at the end of pc,  
relative viscosity, amount of end groups (given in meq per kg of block copolyetherester  
25 elastomer) and overall molecular weights (calculated from the end groups) for block  
copolyetherester elastomers based on different poly(alkylene oxide) polyols.

Example or Comp. Exp./ wt% of poly(alkylene oxide) polyol	PC- time [min]	melt	Torg. [Nm]	$\eta_{rel}$	COOH [meq/kg]	OH [meq/kg]	Unsat. [meq/kg]	Mn [g/mol]
Example I A/65	174	Clear	2.0	3.32	17	18	6.5	48200
Example II A/70	371	Clear	1.9	3.40	18	13	7	52600
Example III B/60	113	Clear	2.0	3.10	13	31	5.4	40500
Example IV B/70	183	Clear	2.0	3.54	14	24.6	6.3	44500
Example V B/75	217	Clear	2.0	3.78	14	21.5	6.8	47900
Comp. Ex. 1 B/50	90	Clear	2.0	2.73	12	44	4.5	33100
Comp. Ex. 2 C/55	185	Clear	2.2	2.75	16	26	20	32300
Comp. Ex. 3 D/80	440	Milky	0.6	2.82	8	37	46	22000
Comp. Ex. 4 E/70		Milky	1.6	3.3	10	21	7	52600
Comp. Ex. 5 E/75	263	Milky	1.4					
Comp. Ex. 6 E/80	315	Milky	1.2	3.3	8	25	8	48800
Comp. Ex. 7 F/65	253	Clear	1.6	3.15	17	16.2	17.6	39400
Comp. Ex. 8 F/70	198	Clear	1.0	2.62	16	24.9	18.9	33400

Contrary to poly(alkylene oxide) polyols D and E, the poly(alkylene oxide) polyols A-C and F gave a clear melt during polymerization, indicating that for A-C and F the balance between the PBP length and amount of PEO in the poly(alkylene oxide) polyol is met to avoid macrophase separation.

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Thermal Properties of the block polyetherester elastomers

Thermal properties are given in Table 3.

- 5 Table 3: Melting temperature, enthalpy of melting and crystallinity PBT, overall crystallinity of the block copolyetherester elastomer, glass transition temperature and crystallization temperature of PBT, for block copolyetherester elastomers with different poly(alkylene oxide) polyols.

Example or Comp. Exp./ wt% poly(alkylene oxide) polyol	T <sub>m</sub> PBT [°C]	dH PBT [°C]	Cry. PBT [%]	Overall Cry. at RT [%]	T <sub>g</sub> [°C]	T <sub>c</sub> PBT [°C]
Example I A/65	193	11.9	24	8	-64	128
Example II A/70	181	8.3	19	6	-64	111
Example III B/60	203	28.4	49	20	-64	144
Example IV B/70	188	10.1	23	7	-64	122
Example V B/75	175	7.2	20	5	-65	98
Comp. Ex. 1 B/50	212	27.1	38	19	-63	158
Comp. Ex. 2 C/55	201	37.5	58	26	-63	140
Comp. Ex. 3 D/80	178	9.5	33	7	-64	141
Comp. Ex. 4 E/80	171	13.4	46	9	-65	101
Comp. Ex. 5 F/65	193	24.7	49	17	-65	136
Comp. Ex. 6 F/70	183	13.4	31	9	-64	128

10 \*\* assuming a melting enthalpy of 100% crystalline PBT of 144,5 J/g. [7]

The PBT crystallization for all materials is clearly determined by the average length of

the PBT blocks. With increasing amount of soft block and decreasing length of soft block the melting temperature decreases. Along with the melting temperature also the PBT crystallinity and the crystallization temperature decrease reflecting the difficulties of the crystallization process of short, diluted PBT segments.

- 5 For some application like e.g fiber spinning a high crystallization temperature is crucial. Therefore it was attempted to increase the crystallization temperature by addition of a nucleating agent. Addition of 0.1% microtalc (Imifabi HTTP Ultra 5C talk) during injection moulding (dryblend) to B/75 lead to an increase of the crystallization temperature from 100°C to 140°C, which is the same crystallization temperature as that
- 10 of C/55 (Table 4).

Table 4: Melting temperature, enthalpy of melting and crystallinity of PBT, overall crystallinity, glass transition temperature and crystallization temperature of PBT for B/75 after 48 h of postcondensation at 170°C and after addition of 0.1% talc (dryblend).

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Example/Comp. Ex./ wt% poly(alkylene oxide) polyol	H	T <sub>m</sub> PBT [°C]	dH PBT [°C]	Cry. PBT [%]	Overall Cry. at RT [%]	T <sub>g</sub> [°C]	T <sub>c</sub> PBT [°C]
B/75	2nd	175	7.2	20	5	-65	98
B/75 +48h SSP	1 <sup>st</sup>	184	13	36	9		
	2 <sup>nd</sup>	182	6.4	16	4	-63	113
B/75 + talc	2 <sup>nd</sup>	173	8.1	24	6	-63	199

#### Mechanical Properties of the block polyetherester elastomers

- Table 5 shows an overview of the mechanical properties of the new Arnitels based on
- 20 different P-type soft blocks.

Table 5: Mechanical data of the new Arnitels based on different soft blocks, measured according to ShoreA hardness) and ISO 527-2 (others).

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Example or Comp. Exp./ wt% poly- (alkylene oxide) polyol	Hardness [Shore A]	E' [Mpa] at 23°C	Yield stress [MPa]	Tensile strength [MPa]	Strain at break [%]	Plastic strain at 100%	Plastic strain at 500%
Example I A/65	87	28	4.0	18.4	1090	16	168
Example II A/70	83	20	3.1	13.9	1360	14	153
Example III B/60	91	45	5.0	21.1	930	17	182
Example IV B/70	84	20	3.1	16.2	1300	13	149
Example V B/75	79	10	2.2	11.8	1470	12	133
Comp. Ex.1 B/50	95	88	7.0	24.1	750	23	239
Comp. Ex.2 C/55	93	55	6.8	23.7	890	22	253
Comp. Ex.3 D/80	not measured	6	not measured	not measured	75	11	-
Comp. Ex.4 E/80	not measured	5	not measured	not measured	250	9	-
Comp. Ex.5 F/65	87	26	4.0	17.8	1110	15	172
Comp. Ex.6 F/70	81	20	3.1	8.6	1120	15	162

#### Moisture vapor transmission rate

5 Tables 6 shows the results of the moisture vapour transmission rate (MVTR) tests according to ASTM E96B (wet cup) and E96BW (inverted cup). For comparison, the values of Sympatex and PL380 are given.

10 As expected the MVTR increases with increasing amount of soft block and increasing amount of PEO in the soft block. The materials P3000/65 and P3000/70 show comparable MVTR as Sympatex, while P3300/70 and P3300/75 even show a higher moisture vapor transmission rate compared to Sympatex.

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Table 6. Results of the MVTR measurement according to ASTM E96B and E96BW  
(38°C, 50% rel. humidity)

Example or Comp. Exp./ wt% poly(alkylene oxide) polyol	Wt% SB	Mn SB [g/mol]	Wt% PEO	Thickness [ $\mu\text{m}$ ]	MVTR (E96B) [g.mm/m <sup>2</sup> .day]	MVTR (E96BW) [g.mm/m <sup>2</sup> .day]
Example I A/65	65	3000	45	77	118	632
				84	117	652
Example II A/70	70	3000	45	72	112	760
				94	134	803
Example III B/60	60	3300	50	80	115	913
				77	115	901
Example IV B/70	70	3300	50	83	131	1392
				90	140	1344
Example V B/75	75	3300	50	83	139	1447
				78	133	1522
Comp. Ex.1 B/50	50	3300	50	69	88	520
				71	93	485
Comp. Ex.2 PL380	55	2300	30	68	74	167
				91	87	169
Comp. Ex.7 F/65	65	2800	40	88	106	397
				84	110	391
Comp. Ex.8 F/70	70	2800	40	60	95	457
				74	109	489
Comp. Ex. 9 Sympatex	30	4000	100	120	114	712

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Claims

1. Block copolyetherester elastomer comprising polyester blocks and poly(alkylene oxide) polyol blocks, obtainable by esterification of at least one aromatic dicarboxylic acid or an ester-forming derivative thereof, at least one alkylene diol, and a poly(alkylene oxide) polyol, comprising a poly(propylene oxide) end capped with ethylene oxide, characterized in that
  - a. the poly(alkylene oxide) polyol has a Mn of between 2500 and 5000 g/mol;
  - b. the poly(alkylene oxide) polyol has an ethylene oxide content of between 22 and 90 % by weight;
  - c. in the block copolyetherester elastomer the ratio by weight of poly(alkylene oxide) polyol/ aromatic dicarboxylic acid or the ester-forming derivative thereof is between 60/40 and 90/10;
  - d. the average degree of polymerization of the polyester block is at least 3.5;
  - e. the block copolyetherester elastomer has a an unsaturation content, being the total content of vinyl and allyl groups, of less than 25 meq per kg of the poly(alkylene oxide) polyol.;
  - f. the block copolyetherester elastomer has an Mn of at least 25,000 g/mol.
2. A block copolyetherester elastomer according to claim 1, wherein the poly(alkylene oxide) polyol has an Mn of between 3000 and 5000.
3. A block copolyetherester elastomer according to claim 1 or claim 2 having a vinyl content of less than 15 meq per kg of the poly(alkylene oxide) polyol.
4. A block copolyetherester elastomer according to any one of claims 1-3 having a Mn of at least 35,000 g/mol.
5. A block copolyetherester elastomer according to any one of claims 1-4 wherein the aromatic dicarboxylic acid or the ester-forming derivative thereof is butylene terephthalate.
6. A block copolyetherester elastomer according to any one of claims 1-5 wherein the alkylene diol is 1,4-butene diol.
7. Process for the preparation of a block copolyetherester elastomer comprising polyester blocks and poly(alkylene oxide) polyol blocks, wherein at least one aromatic dicarboxylic acid or an ester-forming derivative thereof, at least one alkylene diol, and a poly(alkylene oxide) polyol, comprising an poly(propylene



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- oxide) end capped with ethylene oxide, are esterified, characterized in that
- a. the poly(alkylene oxide) polyol has an Mn of between 2500 and 5000 g/mol;
  - b. the poly(alkylene oxide) polyol has an ethylene oxide content of  
5 between 22 and 90 % by weight;
  - c. in the block copolyetherester elastomer the ratio by weight of poly(alkylene oxide) polyol/aromatic dicarboxylic acid or an ester-forming derivative thereof is between 60/40 and 90/10;
  - d. the average degree of polymerization of the polyester block is at least  
10 3.5;
  - e. the poly(alkylene oxide) polyol has an unsaturation content, being the total content of vinyl and allyl groups, of less than 25 meq per kg;
  - f. the block copolyetherester elastomer has an Mn of at least 25,000 g/mol.
- 15 8. Process according to claim 7, wherein the esterification reaction is performed in the presence of up to 6.0 equivalents per 100 moles of dicarboxylic acid of a diisocyanate.
  9. Use of a block copolyetherester elastomer according to any one of claims 1-6 in an elastic fiber.
  - 20 10. Use of a block copolyetherester elastomer according to any one of claims 1-6 in an elastic film.
  11. Use according to claim 10, wherein the elastic film is breathable.
  12. Product comprising at least one block copolyetherester elastomer according to any one of claims 1-6.
  - 25 13. Product according to claim 12, the product being an elastic fiber.
  14. Product according to claim 12, the product being an elastic film.

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ABSTRACT

- The invention relates to a block copolyetherester elastomer comprising polyester blocks and poly(alkylene oxide) polyol blocks, obtainable by esterification of at least one aromatic dicarboxylic acid or the ester-forming derivative thereof, at least one alkylene diol, and a poly(alkylene oxide) polyol, comprising an poly(propylene oxide) end capped with ethylene oxide, wherein
- a. the poly(alkylene oxide) polyol has an Mn of between 2500 and 5000 g/mol;
  - b. the poly(alkylene oxide) polyol has an ethylene oxide content of between 22 and 90 % by weight;
  - c. in the block copolyetherester elastomer the ratio by weight of poly(alkylene oxide) polyol/ aromatic dicarboxylic acid or the ester-forming derivative thereof is between 60/40 and 90/10;
  - d. the average degree of polymerization of the polyester block is at least 3.5;
  - e. the block copolyetherester elastomer has a an unsaturation content, being the total content of vinyl and allyl groups, of less than 25 meq per kg of the poly(alkylene oxide) polyol;
- the block copolyetherester elastomer has an Mn of at least 25,000 g/mol.

1/1

Fig.1

